

ART. III.—*On the Essential Oil of Boronia pinnata, Sm.
and the presence of Elemicin.*

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[Read 10th July, 1919].

The Boronias (N. O. Rutaceae) are plentifully distributed in Australia, and constitute a genus the flowers of which are often strongly perfumed.

The essential oil, the subject of this communication, was distilled by Mr. P. R. H. St. John, in Melbourne, from material collected, towards the end of the year 1917, in the Longwarry District of Victoria. The plant at that time of the year was in full bloom.

Very few species of *Boronia* have so far been worked for their oil, and consequently little is at present known concerning the constitution of their odoriferous products.

In this case it is particularly interesting to know that almost three-fourths of the oil consists of the trimethoxy-phenol ether, Elemicin.

This substance which is 4-allyl-1,2,6, trimethoxy-benzol; $C_{12}H_{16}O_3$, occurs in the higher boiling portion of the oil of Manila Elemi, and it was from this oil that it was first isolated, and its characters and composition determined.

The constants given for Elemicin are:—boiling point 144-147°C. at 10 millimetres pressure; density at 20° = 1.063, refractive index 1.5284; also that it occurs in the fraction of the oil boiling at 277-280°C.

The oil of *Manila Elemi*, distilled from the oleo-resin of *Canarium commune*, L., is thus derived from plants belonging to the Burseraceae, a natural order somewhat far removed, systematically, from the Rutaceae, to which *Boronia* belongs, and it is thus interesting to find this rare plant constituent so widely distributed.

The slight fluorescence of the oil is also worthy of remark, because it seems very probable that this was wholly or partly due to the presence of a small quantity of the methyl-ester of anthranilic acid, which constituent it was possible to extract from the oil by agitating with dilute sulphuric acid. As the plant was in flower at the time of distillation, it is probable that this ester

was derived from the flowers, and it may be found not to occur in the leaves. Although the fluorescence of the oil was apparently considerably diminished after agitation with dilute acid, yet it was not entirely removed in this way.

A considerable amount of work has been carried out on elemicin, and iso-elemicin, by Semmler (Ber. 1908, 41, 1768, and other references in the same volume), the material worked upon having been derived from Eleni oil.

This is the first time elemicin has been detected in the oils of Australian plants.

My thanks are due to Mr. F. W. Byrne, of the Chemical Department of the Museum, for assistance in this investigation.

Experimental.

The total yield of oil was equal to 0.383 per cent. The crude oil, which was heavier than water, was of a light amber colour, and had a mild aromatic odour, suggesting the presence of geraniol and geranyl-acetate. It also had a slight fluorescence. When dissolved in absolute alcohol the secondary odour was pleasant, and it appears that the oil of this species of *Boronia* will be found a useful addition to the perfumery products of Australia.

The crude oil had :—

Specific gravity at 15°C. = 1.0197.

Rotation $\alpha_D = +3.8^\circ$.

Refractive index at 20°C = 1.5125.

Soluble in 1 vol. 70 per cent. alcohol (by weight).

The dextrorotation of the oil was due to the activity of a small quantity of pinene; this is shown later.

The saponification number for the esters was determined both by boiling and in the cold.

(a) 1.5252 grams boiled for half-an-hour with alcoholic potash, required 0.0308 gram KOH. S.N. = 20.2.

(b) 1.528 grams treated with alcoholic potash in the cold with two hours' contact required 0.028 gram KOH.

S.N. = 18.3.

This result is important, and, together with the odour, indicates that the chief ester in the oil is geranyl-acetate, and that it occurs to the extent of 6.4 per cent.

That free geraniol was also present is suggested from the results of acetylation. A portion of the crude oil was boiled with acetic anhydride and anhydrous sodium acetate in the usual way.

- (a) 1.5144 grams of this esterised oil, when boiled with alcoholic potash, required 0.056 gram KOH. S.N. = 36.9.
- (b) 1.5162 grams, when treated with alcoholic potash in the cold, with two hours' contact, required, 0.042 gram KOH. S.N. = 27.7.

To confirm this result some cold saponified oil was steam distilled. Besides the terpenes an aromatic alcohol came over, which was strongly indicative of geraniol.

Although the chief alcohol may be considered to be geraniol, yet it is evident that other alcohols were also present.

Determination of Combined Acids.

A portion of the crude oil was boiled for two hours with an aqueous solution of sodium hydroxide. The alkaline solution was separated and acidified with sulphuric acid. The clear filtered solution was distilled until volatile acids ceased to come over. The distillate was neutralised with Barium hydrate solution, evaporated to dryness and treated in the ordinary way.

- (a) 0.1868 gram Barium salt gave 0.1580 gram BaSO_4 = 84.58 per cent.
- (b) 0.2306 gram Barium salt gave 0.1958 gram BaSO_4 = 84.91 per cent.

On treating the Barium salt with sulphuric acid the odour of butyric acid was noticeable; it is thus assumed that butyric acid was also present. The results obtained are equal to 59.8 per cent. of Barium acetate, and 40.2 per cent. Barium butyrate. The acetic acid was evidently in combination with the geraniol as geranyl-acetate.

The amount of free acid in the crude oil could not be satisfactorily determined for several reasons, and although a small amount of a solid acid was eventually isolated, yet the saponification number was under 2.

Phenol and Free Solid Acid.

A portion of the oil was shaken with dilute sodium hydroxide until extraction was complete. The aqueous solution was separated, shaken with ether to remove adhering oil, acidified, and again shaken with ether. The ether extract thus obtained was equal to 0.198 per cent., and was semi-crystalline, due to the presence of the solid acid.

The product was dark coloured, and had a strong phenolic odour. It was dissolved in ether, and the acid removed from the phenol by shaking with a solution of Sodium carbonate. The small quantity of acid when finally purified, was crystalline, and melted at 159-160°C. It was not cinnamic acid, and perhaps consisted of trimethylgallic acid, which is formed by oxidation of elemicin.

The ether solution of the phenol after removal of the acid was evaporated to dryness. The residue had a strong phenolic or creosote-like odour, was not crystalline, and when dissolved in alcohol gave a purplish-brown colour with ferric chloride, which colour remained persistent.

Tests for some of the well-known phenols gave negative results, and as the amount was small, its identity could not be determined.

The oil, after the removal of the phenol and free acid, was repeatedly shaken for some days, with a saturated solution of sodium bisulphite, but no combination took place. Aldehydes were thus absent.

Distillation of the Crude Oil.

100 c.c. of the crude oil were submitted to distillation under atmospheric pressure. A few drops of an acid water with a little oil came over below 160°C. (uncorrected). Between 160-250° only 16.5 c.c. came over as first fraction, 10 c.c. of which distilled below 180°.

This temperature rose rapidly to 259°, and distillation then proceeded as follows:—

259-265° = 18 c.c.

265-270° = 50 c.c.

270-274° = 63 c.c.

274-280° = 70 c.c.

This fraction was then separated, and although 3 c.c. of an oil came over on continued heating, yet the temperature did not rise beyond 280°. The residue in the still was a dark hard pitch-like substance, which powdered readily when cold.

The first fraction gave the following results:—

Specific gravity at 15°C. = 0.8657.

Rotation $^aD = +15.9^\circ$.

Refractive index at 20° = 1.4639.

Cineol was not present. The oil of this fraction was fluorescent.

15 c.c. of the first fraction were again distilled, when 7.5 c.c. came over below 158°C., and 5.5 c.c. between 158-190°. The

portion distilling below 158° had

Specific gravity at $15^{\circ} = 0.8596$.

Rotation $^{\alpha}D = +21.2^{\circ}$.

Refractive index at $20^{\circ} = 1.4569$.

and formed a nitrosochloride, which melted at $104^{\circ}C$.

The lower boiling constituent in the oil was thus shown to be dextrorotatory pinene.

Possibly limonene was also present in the intermediate portion, as the specific gravity was only 0.8590.

The second, or large fraction, gave the following results:—

Specific gravity at $15^{\circ}C. = 1.0519$.

Rotation $^{\alpha}D = +0.4^{\circ}$.

Refractive index, at $20^{\circ} = 1.5230$.

Soluble in 0.5 volume of 70 per cent. alcohol, remaining clear on further addition.

After removal of any phenol which might be present in this fraction, it was again distilled under reduced pressure, the first 15 c.c. being discarded. The remainder boiled fairly constant at $191^{\circ}C$. under 47 millimetres pressure. The product gave the following results:—

Specific gravity at $20^{\circ}C. = 1.0705$.

Inactive to polarised light.

Refractive index at $24^{\circ}C = 1.5283$.

It was thus considered that the bulk of the oil consisted of this constituent. When freshly distilled, it was practically colourless, had a slight fluorescence, and a delicate aromatic odour, reminding somewhat of linalool. It darkened slightly on keeping.

Analysis gave the following:—

(a) 0.1688 gram gave 0.1196 H_2O ; and 0.4222 CO_2 : $H = 7.87$ and $C. 68.22$ per cent.

(b) 0.1332 gram gave 0.0932 H_2O ; and 0.3362 CO_2 : $H = 7.8$ and $C. 68.85$ per cent.

$C_{12}H_{16}O_3$ requires $H. 7.75$ and $C. 69.1$.

Methoxy Determination.

(a) 0.2872 gram gave 0.9498 AgI equal to 43.6% OCH_3 .

(b) 0.3144 gram gave 0.9939 AgI equal to 41.8% OCH_3 .

It is thus evident that the molecule $C_{12}H_{16}O_3$ contains three methoxy groups.

That the molecule was unsaturated was shown by the action of Bromine, when the substance was dissolved in carbon tetrachloride,

although a satisfactory bromide was not obtained. At first the bromine was absorbed without evolution of hydrobromic acid, but later the evolution of HBr. was pronounced, the solution becoming dark purple.

Formation of the Acid.

A portion was oxidised by Potassium permanganate in alkaline solution; considerable heat was evolved. After completion of the reaction, the remaining colour was removed by sulphurous acid, filtered, evaporated to small bulk, and acidified with dilute sulphuric acid. A solid acid separated at once. This was purified from boiling water, from which it crystallised in needles. It melted sharply at 169°C (corr.) without decomposition. The acid was titrated with decinormal sodium hydroxide; 0.13 gram dissolved in absolute alcohol required 6.15 c.c. $\frac{1}{10}$ NaOH to neutralise, thus 40 grams would neutralise 211.4 grams of acid, $\text{C}_{10}\text{H}_{12}\text{O}_5 = 212$.

It was thus evident that the acid was trimethylgallic acid $\text{C}_{10}\text{H}_{12}\text{O}_5$, the characteristic acid formed by the oxidation of elemicin.

That a small quantity of iso-elemicin was also present was indicated by the formation of a minute quantity of acetic acid on oxidation by Potassium permanganate. This was shown by distilling over the free acid and forming with it the Barium salt. This on ignition gave 91.6 per cent. BaSO_4 . Theory requires 91.37 per cent.

The above investigation shows that the principal constituent in the oil of *Boronia pinnata* is the trimethoxyphenol-ether, Elemicin. (4 allyl—1,2,6 trimethoxybenzol) and that it occurs in the oil of this species to the extent of about 70 per cent.